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Environmental Cleanup Office

Date: March 9, 1998
To: Mary Kay Voitella
From: Orville Kiehn,
EPA Environmental Engineer
Mining Engineer
Mineral Process Engineer
EPA Region 8

Thank you and Mr. Jim Stefanoff of CH2MHill (HILL) for all considerations in the arrangement of my trip to Spokane for the Bunker Hill Workshop March 2-3 and for the Bunker Hill Mine and surface facilities tour on March 1st. These kind considerations greatly assisted my understanding of the mine, the mine setting and geography, an appreciation of the significant accumulation of snow in the drainage above the site and gave me an opportunity to visit with and understand some of the operations and maintenance challenges of the mine owner and operator, Mr. Bob Hopper.

I called Jim Stefanoff on March 8 for Mr. Hopper's mailing address. Mr. Hopper and I agreed to exchange ore specimens, his of argentiferous galena-sphalerite ore (Ag-Pb-Zn) from Bunker Hill for my argentiferous digenite (Ag-Cu) from the original Kennecott Mine in Alaska.

The Bunker Hill Mine

The following are my comments on my Bunker Hill Mine & surface facilities tours on March 1, 1998 accompanied by Mr. Jim Stefanoff of HILL:

Mr. Hopper provided a tour of the underground mine 9 level. We accessed the mine via the Kellogg Tunnel (Tunnel) (actually a haulage/man access adit) on a electric loci along the 9KT Flume to the 9LA Flume and #2 raise locations. Inbound and outbound we viewed the condition of the flumes, the Kellogg Tunnel back, floor and ribs, tunnel drifts, the obvious presence of iron hydroxide "yellow boy" in the flume and the precipitous condition on the Tunnel back, specifically in the faulted and fractured zones. Mr. Hopper explained the significant amount of work that was required to initially enter, recondition, repair and maintain just a fraction of the total mine. We were shown one hoist system that had been reconditioned. Very well done! The mine areas he described are important to his current approximate 500 tpd operations in the underground mine workings.

He advised certain other work remained in the effort to return more of the mine to a operating condition including the reconditioning of hoisting equipment that we viewed. This equipment escaped the attack of scavengers who tore apart and carried off so much of the rest of the mine equipment and wiring. He was thankful that the equipment casting molds were saved yet unhappy that other mine equipment reportedly in secured storage under EPA control was lost.



From a current maintenance perspective, the ongoing requirements of maintaining mine access via Tunnel and drift repair, water management & manual flume/ditch cleaning require a constant application of resources (money, manpower and materials). Mr Hopper advised that one historic spring freshet deluge flushing of the upper or "upcountry" workings resulted in nearly a year of extensive cleanup in the operating lower mine levels. Mr. Hopper reported that mine operations ceased during this cleanup period. I reflect at this point on what was reported to me by Jim Stefanoff as a record snow accumulation above the site.

I developed an understanding from Mr. Hopper that given the opportunity to sell the mine- he would accept a reasonable offer. He advised that a significant rise in price of any of the three products (lead, zinc & silver) would make the mine profitable and appealing to a prospective buyer. Considering the present state of depressed commodity prices and given the opportunity to go back in time (when he considered purchasing the mine)-he advised that he would decline the offer. These are my understandings of our conversation.

Considering the magnitude and probable in-perpetuity duration of a 2nd and 3rd party operation of this site (EPA and the State of Idaho), it would behoove the regulators to continue (as you have very properly done to date) to provide resources that assist Mr. Hopper (technical evaluation of water management means to abate surface water origin mine inflow and mine pool storage of low-flow period mine inflow; technical evaluation of optimum water treatment means to meet draft TMDLs; technical evaluation of sludge management to minimize waste handling and identification of cost effective long term site storage) so that he is somewhat encouraged to continue to be actively involved in the Bunker Hill mine maintenance and surface water treatment. I applaud your approach!

As you very well understand, these mine takeovers by regulators are costly. For example, similar (operating costs only) activities at the Colorado Summitville Mine site presently cost EPA and the taxpayers approximately \$2.5 million/year per Victor Ketellapper, EPA Region 8 Remedial Project Manager. To date, Summitville has cost the taxpayers \$130 million with \$20-25 million designed and planned for reclamation by 2001. Added to this capital is the aforementioned \$2,5 million/year operations burn rate.

Undoubtably Region 10 understands EPA's financial burden at the California Iron Mountain Superfund site in EPA Region 9. Jim Stefanoff of HILL, having worked there, understands it as well.

The Surface Facilities

The Kellogg Tunnel discharges an annual average flow of 1500 gpm of pH 2-4 metal leaching/acid rock drainage (ML/ARD) via a 24"-20" series coupled pipeline to a 7.5 million gallon surge pond. The surge pond is sequentially pumped (a pumping lift being required) to a decades-old water treatment facility, the Central Treatment Plant (CTP). The outdoor lime-addition CTP raises the pH of the influent water in a violently agitated mixer and settles the sludge in a large clarifier-thickener. The water treatment monitoring system was advised by Mr.

Stefanoff to be inoperative. No effluent filtration system is installed. Several design modifications of the CTP linked to projected average end-of-pipe effluents are presently in consideration by the staff of HILL. The surface facility analysis work appears to be very well thought out, staffed, managed and very well directed by EPA Region 10.



The clarifier effluent current NPDES permit discharge requirements are less strict than the draft TMDL for total lead, zinc and cadmium by one to two orders of magnitude, assuming 50% river flow conditions. Nick Ceto, in a aside, kindly explained some of the Bunker Hill site TMDL background developments being addressed by your R10 water group. I continue to harbor the belief that we (all Regions) need to better understand the TMDL background and process (and what data and facts are important in the process) so that we have an expert knowledge in discussing TMDLs with the States, other regulatory agencies and the public.

The clarifier sludge is piled on the partially reclaimed mill tailings impoundment. The impoundment or Central Impoundment Area (CIA) was advised to total approximately 200 acres. Approximately 6-7 years of current sludge production has been estimated by HILL to fill the CIA. HILL is evaluating sludge management options including the production of salable by-products.

In the Workshop discussion on March 3rd I understood that if approximately 50% of the sludge volume could be sold tomorrow (most or all of the present non-salable iron hydroxide has no present market and would remain on the site), the site storage capacity could be extended to double that projected at present or 12-14 years.

☺-I like what I hear and see in the directed work of your contractor **CH2MHILL**! I do have a few comments which follow:

Comments:

Mine

1. In regards source control of possible mine inflow waters (presently ephemeral surface flows that per John Riley may enter the mine via a fractured zone upgradient of the Guy Cave Area), I have briefly discussed the BH Mine with our Region 8 Hydrologist-Geologist Mr. Mike Wireman, advising Mike that he can expect a call from John. Mike has had recent good experience and

results at several fractured rock hard rock mine sites, identifying underground groundwater flowpaths using the ground water isotope tracing services of Hydrologist Mr. Gareth Davies, Cambrian Ground Water Company of Oak Ridge, Tennessee. Mike Wireman's phone number is 303-312-6719.

Mike has experience with both the USGS's Dr. Bryant Kimball (801-975-3384) out of their Salt Lake office and Mr. Davies. Bryant's work is similar to that of Mr. Davies but involves any one or more of several salt tracers (sodium chloride, potassium chloride, bromine chloride, etc.).

Both approaches involve injection of the tracer/s in groundwater wells, streams, etc. and downgradient monitor of surface streams for the isotope/element of interest. At Bunker Hill, the monitor could be a water sampling at a strategic underground mine water discharge location.

2. In Colorado we are aware of two catastrophic mine water discharges that have either (1) narrowly missed (middle of the night) drowning mine workers (At the Sunnyside Mine site, Lake Emma, following a catastrophic collapse of mine workings, flooded the workings and discharged the debris out the American Tunnel) or (2) flooding workings that killed mine workers (Argo Tunnel mine workings- ML/ARD metal hydroxide-originated dam failure and subsequent water release). I discussed this concern with Mr. Hopper. He acknowledged this catastrophic type of mine flooding as a Bunker Hill Mine possibility.

With the present BH Mine upper country surface forested area now covered with a near record snow pack, suggested is extreme caution, especially during the freshet part of the hydrograph, for any mine exploration and evaluation of surface inflows in the Flood-Stanly area.

3. Noted was absence of a discussion biological importance in ML/ARD reactions in the Prescriptive Remedy text (2.0 Background, 2.1 General AMD Production Process, page 2) which conflicts with Figure 4-1, Chemistry of Acid Production., presented in the AMD Conceptual Model, etc. presented by Germon & Riley on March 2, 1999 at the Workshop. On page 2 of the Prescriptive Remedy text the statement is made to the effect that but three contributing components drive the chemical reaction: e.g. pyrite-rich ore, oxygen, and water. Is it possible, perhaps very possible, that in the presence of these three contributing components that the additional presence of a thiobacillus ferrooxidans-type bacteria is what actually drives the reaction at an-exponential rate?

This possibility then leads to the question of the possible cost-effective application of a bactericide, which discussion at the Workshop led to a conclusion that experience has shown it to be non-cost-effective in surface applications. It was verbally concluded that underground application would be an order-of-magnitude more difficult. Suggested is a discussion in a applicable section of the text of the oxygen-assisted activity of the bacteria and alternatives for the control of this activity that have been considered and dismissed.

4. Discussed was the injection of upcountry low pH mine water into the higher pH lower country mine pool that had been tested by Mr. Hopper at a depth of about 200 feet below the pool surface. This injection resulted in precipitate flocs rising to the pool surface. Mr. Hopper advised

a desire to retest injection at a depth of approximately 400 feet below the pool surface. Mr. Hopper advised that this evaluation was not done.

This discussion began with advice by Jim Stefanoff of receipt of a Butte, MT successful evaluation of a limed pond approach for treatment of ML/ARD. The report on the test results forwarded by O. Kiehn and was earlier forwarded by Mr. Edward R. Bates, START Leader, Site Management Support Branch, the EPA Cincinnati Risk Management Research Laboratory to EPA R10 Remedial Manager Victor Ketellapper for consideration at Summitville.

The prospects of either injecting upper country water at some depth in the mine pool or with a mechanical device (I forget the name) that initially injects lime into the stream to be subsequently injected in the mine pool is intriguing. The possibility is that floc formation and resulting sludge deposition could take place in up to 18 levels below the present mine pool surface. A number of issues might be addressed as a result of such a process: (a) obviously reduction of the volume and tonnage of sludge deposited on the surface; (b) by virtue of the buildup of the sludge, a type of plug, a proportional reduction of the underground inflow of water from the Crescent Mine into the mine pool; (c) reduction in the cost and use of lime and other reagents; (d) reduction in the concentration of metals pumped to the CTP, leading to a possible change to a more effective/efficient flowsheet design to better meet TMDL requirements; (e) the use of a large area of the CIA for other purposes such as a ballpark.

The Surface Facilities

(1) The HILL staff did an excellent job in presenting the conventional options available in the in the treatment of ML/ARD. The presentations were clear and concise and very understandable for someone both experienced in the field and for non-technical background folks as well.



(2) In the HILL presentation on alternative technologies, I was asked to discuss my knowledge of the bioreactor alternative by Jim Stefanoff. This technology is new, "cutting edge" so to speak, an engineered development progress of what was first termed in the literature "wetland treatment", then "constructed wetlands" and as the technology developed, "bioreactor/s". The bioreactor technology/technical papers on the newest successful developments are to be mailed under separate cover to you, and in response to requests, to Nick Ceto of R10, Robert York of HILL and Nick Zilka, Idaho's DEQ On Site Coordinator.

If additional bioreactor information is of interest, a call to Mr. Jim Gusek of Knight-Piesold LLC in Denver, CO is suggested. His phone number is 303-626-8788; Fax 303-629-8789; Email jimg@kpco.com ; Web site: www.knightpiesold.com.

Also, suggested is a second source of bioreactor information: Mr. Andre de Vegt, Paques, Inc., in Exton, PA. His phone number is 610-363-9564; Fax 610-363-9554; Email adevegt@paquesusa.com

THE CHALLENGES OF DESIGNING, PERMITTING AND BUILDING A 1,200 GPM PASSIVE BIOREACTOR FOR METAL MINE DRAINAGE WEST FORK MINE, MISSOURI¹

James Gusek, P.E.², Dr. Thomas Wildeman³, Aaron Miller⁴ and James Fricke⁵

Abstract. An active underground lead mine produces water having a pH of 8.0 with 0.4 to 0.6 mg/L of Pb and 0.18 mg/L of Zn. A full-scale 1,200 gpm capacity bioreactor system was designed and permitted based on a phased program of laboratory, bench and pilot scale bioreactor testing; it was constructed in mid-1996. The gravity flow system, covering a total surface area of about five acres (2 ha), is composed of a settling basin followed by two anaerobic bioreactors arranged in parallel which discharge into a rock filter polishing cell that is followed by a final aeration polishing pond. The primary lead removal mechanism is sulfate reduction/sulfide precipitation. The discharge has met stringent in-stream water quality requirements since its commissioning. The system was designed to last about 12 years, but estimates suggest a much longer life based on anticipated carbon consumption in the anaerobic cells.

Key words: Metal Mine Drainage, Lead, Zinc, Passive Treatment, Anaerobic Bioreactors

Introduction

Asarco's West Fork Unit is an underground lead-zinc mine that discharges water from mine drainage to the West Fork of the Black River (West Fork) under an existing NPDES permit. The adoption of water quality based discharge limits in its NPDES permit issued in October, 1991, prompted Asarco to evaluate treatment methods for metal removal.

Evaluations of alternative treatment processes determined that biotreatment methods were feasible and cost less than half as much as sulfide precipitation. The goal of the water treatment project was to ensure that the stringent water quality based limits in the permit would be consistently met.

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Location

The West Fork Unit is located in Reynolds County in central Missouri, about three hours from St. Louis (Figure 1). The mine is located in the New Missouri Lead Belt.

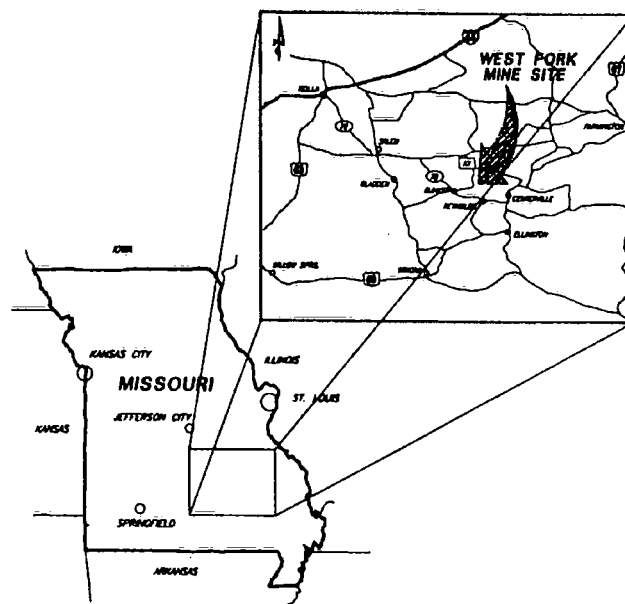


Figure 1, Site Location

Flow rates in West Fork vary from about 20 cubic feet per second (cfs) to more than 40 cfs; water quality is relatively good, despite being located in an area with naturally high background levels of lead due to the bedrock geology. The mine discharges about 1,200 gpm

on the average (2.7 cfs) or about 10 percent of the total flow in West Fork.

Biotreatment

A Brief History of Biotreatment

Natural systems have been removing metals from water for eons; examples include pyrite fixed into coal beds and bog iron ore deposits. For the past 10 years, wetlands and bogs have been the natural method of choice for improving water quality. Contaminant reductions are being seen through the precipitation of hydroxides, precipitation of sulfides, and pH adjustments. Local conditions, oxidation state, and water and soil chemistries dictate whether such natural reactions occur under oxidizing (aerobic) or reducing (anaerobic) conditions. Man-made or constructed wetlands/bioreactors employ the same principles as natural wetlands, but are designed to optimize processes occurring naturally in wetland ecosystems. Aerobic and anaerobic zones occur in natural wetlands (Figure 2) (Wildeman, et al., 1993). The key goal of bioreactors/wetlands is the long term immobilization of metals in the substrate materials. Metals are precipitated as carbonates or sulfides in the bioreactor substrate (anaerobic cells) and as oxides in aerobic (rock filter) cells.

Anaerobic bioreactors have been successful at substantially reducing metal concentrations and favorably adjusting pH on metal mine drainages. It is generally

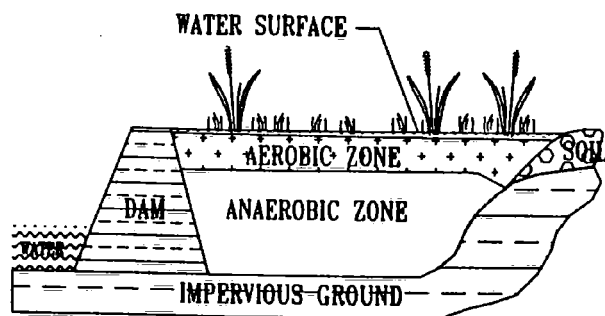


Figure 2, Natural Wetland Ecosystem Zones

recognized that the bacteria commonly found in cattle and other domestic animal intestinal tracts include sulfate reducers and a consortium of other beneficial bacteria. Hence, cow or other animal manures have been frequently used as bacterial inoculum for anaerobic biotreatment cells. These same bacteria are found in many natural wetlands and bogs, and in lakes and ocean

water. Aerobic biotreatment systems are similar to "natural" wetlands in that they typically have shallow depths and support vegetation in the form of algae.

Since the early 1980's, researchers have documented water quality improvements in natural wetland systems. The former US Bureau of Mines (USBM), Tennessee Valley Authority (TVA), and universities such as the Colorado School of Mines [CSM] and others focused on plant-based ecosystems for biotreatment. Many pilot scale systems were built but results were uneven.

In the interval from 1985 to 1988, Greg Brodie of TVA and Bob Kleinmann of the former USBM began to use influent water chemistry as part of the design for aerobic type systems for treating coal mine acid rock drainage (ARD) (Hammer, 1989). In 1987, CSM, Knight Piésold/Camp Dresser & McKee and the US EPA jointly developed a pilot system for metal mine ARD at the Big Five Tunnel in Colorado. At the Big Five Tunnel, anaerobic processes were found to be important in metals removal; macroscopic ecosystems were not needed because the cells worked fine without plants.

Since 1988, there have been rapid advancements in understanding the functioning of wetland/bioreactor systems. The first large scale aerobic system (2,000 gpm capacity) was built in 1992 by TVA; the West Fork Unit system (1,200 gpm capacity) is the first large-scale anaerobic biotreatment system. Aerobic "rock filter" treatment follows for polishing manganese and other parameters.

While the volumetric flow capacity of the West Fork system is a biotreatment milestone, the metal mass loading capacity has been surpassed by many other pilot scale systems which treated water with metal concentrations one thousand times more concentrated than those observed at West Fork. The innovative West Fork technology holds promise over typical chemical treatment methods because large volumes of sludge are not generated; in fact, sludge disposal may be delayed until the end of the project life. In situ reclamation may also be feasible.

Biotreatment Removal Mechanisms

Research has shown that microbial processes are a dominant removal mechanism in anaerobic type biotreatment systems. One prominent researcher calls these systems "bioreactors with green toupees," referring

to the organic substrate where most of the bioreactions occur and the collection of plants that often grow on their surfaces.

Many physical, chemical and biological mechanisms are known to occur within biotreatment systems to reduce the metal concentrations and neutralize the acidity of the incoming flow streams. Notable mechanisms include:

- Sulfide or carbonate precipitation catalyzed by bacteria in anaerobic zones;
- Hydroxide or oxide precipitation catalyzed by bacteria in aerobic zones;
- Adsorption and exchange with plant, soil and other biological materials;
- Filtering of suspended material;
- Metal uptake into live roots and leaves; and
- Ammonia-generated neutralization and precipitation of hydroxides.

Remarkably, some studies have shown that plant uptake does not contribute significantly to water quality improvements in wetlands. This may be plant-species dependent. Plants can, however, replenish the anaerobic bioreactor with organic material and add aesthetic appeal. In aerobic biocells, plant-assisted reactions appear to aid the metal-removal performance of the system, perhaps by increasing oxygen and hydroxide concentrations in the surrounding water through photosynthesis-related reactions that use bicarbonate in the water.

Bacterial Reactions

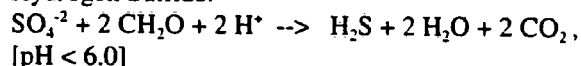
Research testing showed that anaerobic reactions could provide the desired level of lead remediation at West Fork. In the anaerobic systems, sulfide precipitation assisted by sulfate-reducing bacteria thriving in the anaerobic zones has been demonstrated to be the most significant metal removal mechanism. The bacterial reactions involve the generation of

- sulfide ions (S^{2-}), which combine with dissolved metals to precipitate sulfides, and
- bicarbonate, which has been shown to raise the pH or alkalinity of the effluent.

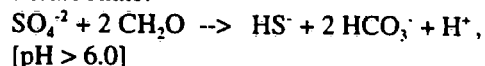
The sulfate reducing bacteria, which appear to function best above pH 5.5, are believed to produce sulfide ions which can in part volatilize into hydrogen sulfide gas (H_2S) and bicarbonate (HCO_3^-) in accordance

with the following reactions:

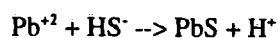
Hydrogen Sulfide:



Bicarbonate:



At low pH, hydrogen sulfide gas bubbles up through the bioreactor substrate, precipitates metals as sulfides, and essentially reverses the reactions that produced the dissolved metals in the water. At higher pH values such as those observed at West Fork, the sulfide ion is in solution and available for precipitation of metals. In the case of dissolved lead, soluble sulfide ion combines to form the lead sulfide mineral galena (PbS):



Testing had also shown that manganese in the anaerobic cell effluent was elevated during the startup period, but then it dropped below 1 mg/L after 40 days of operation. The results of testing also suggested that aerobic reactions would be required in order to polish the discharge from the proposed West Fork anaerobic cell for excess sulfide and for biological oxygen demand prior to discharge. Thus, a brief discussion of aerobic bacterial processes is appropriate.

The primary component of the West Fork aerobic biotreatment system, a "rock filter," re-oxygenates the anaerobic cell effluent as the water passes through the system and serves as a final aeration polishing pond. Excess dissolved sulfide is oxidized from the effluent solution ($S^{2-} + O_2 \Rightarrow SO_4$) in this step. Because the pH is above 7, the evolution of hydrogen sulfide gas is abated. The development of aerobic rock filters for removing dissolved organic matter that create biological oxygen demand (BOD) has been well established in municipal waste water treatment installations. The oxidizing of sulfide from anaerobic bioreactor effluent was documented from the West Fork Unit pilot scale biocell in a "sluice" installed downstream of the biocell. In the rock filter, photosynthesis reactions and open channel flows provide the oxygen needed to remove BOD and oxidize sulfide.

As the water passes through the rock filter, the combined effects of algal growth (especially in the zone surrounding the algae cell wall where pH is high) and the bacteria *Leptothrix discophora* (Robbins et al., 1997) probably precipitate most of the manganese as a black manganese oxide which coats the rocks in the rock filter. This coating is similar to the natural black coatings on rocks observed in many regional streams and ground water intersecting highway cuts throughout Reynolds County, Missouri.

Removal of manganese was projected to be required on a short term basis because its source was the substrate material in the anaerobic cells. The levels of manganese in the effluent of the pilot biocell appeared to approach influent levels after about five months of biocell operation. Removal of manganese in rock filter aerobic cells has been documented in many studies including Wildeman, et al., 1993 and Robbins, et al., 1997.

Test Methods

As with any water treatment facility, the West Fork Biotreatment system was designed by following a phased testing approach that begins in the laboratory and progresses through bench scale and pilot scale systems before sufficient data are gathered to design a full scale passive treatment system. This approach was eventually adopted after Asarco initially constructed and operated a bench scale reactor based on a preliminary design whose results showed promise. A brief history of the design process implemented at West Fork follows.

Asarco had initiated investigations into improving water quality from the West Fork Unit into the West Fork of the Black River as early as 1989. At that time, suspended solids concentrations were the prime concern and numerous test programs were undertaken to minimize suspended solids in the effluent. While improvements were realized through modifications of settling ponds prior to discharge, effluent limits on total lead in the NPDES permit issued in October, 1991 were decreased to levels below which primary settling would work. Asarco initiated investigations into biotreatment and other treatment options to meet lead limits in early 1993 (Knight Piésold, 1995).

The investigations revealed that the unique water chemistry at the West Fork site was not amenable to "standard" water treatment techniques such as pH adjustment, flocculation/settling or sodium sulfide precipitation (which should have worked) for the removal

of lead to meet effluent limits. These standard treatment processes were found to be either impractical or too expensive or could not be made to work in field tests. As such, Asarco utilized its positive experiences with biotreatment at other metal mine sites to focus on a relatively new technology that was innovative and, most important, efficient, as demonstrated by two years of pilot plant performance data.

Water quality modeling using MINTEQAK software suggested that relatively small additions of sulfide under the anaerobic conditions of a biotreatment cell would achieve an effluent with acceptable limits for lead (less than 0.035 ppm). Other removal mechanisms such as lime or sodium carbonate additions did not meet the required treatment levels. Conversely, the biotreatment process is consistent with basic geochemical knowledge and was confirmed by positive pilot scale test results. It was found to be the appropriate process to use to treat West Fork's unique water quality.

Bench Scale and Laboratory Testing

Evolution of the Asarco West Fork biotreatment system design began with bench scale testing. Asarco initiated biotreatment investigations in January, 1993 with the commissioning of a bench scale "bio-tank" system that was operated until February, 1994. The bio-tank, about eight feet in diameter and four feet deep, was initially filled with "green" cow manure; this substrate material was replaced in June, 1993 with a mixture of aged cow manure and aged saw dust. The bio-tank treated up to eight liters per minute (about 2.1 gallons per minute [gpm]) of mine water until it was dismantled. The undepleted substrate was then used to inoculate a larger cell.

In anticipation of pilot scale design, laboratory testing to evaluate other substrate candidate materials was undertaken in August and September, 1993. From October through November, 1993, an evaluation of the laboratory and bio-tank performance results yielded a pilot scale system design which was approved by Asarco in November of 1993. Adverse weather prevented pilot scale construction until February, 1994.

Pilot Scale Field Testing

The pilot scale system was commissioned at an outdoor site adjacent to the mine in March, 1994; it reached design flow (20 gpm) and removal rates in about June, 1994 and operated successfully at a nominal rate of

about 25 gpm with flows as high as 49 gpm providing high-end operating data until February, 1996. Several polishing-type aerobic cells were added in parallel to evaluate the removal of manganese, BOD, fecal coliforms, and sulfide removal and the enhancement of dissolved oxygen in the system effluent.

Interim bench scale studies were undertaken while the pilot system was operated. These studies evaluated startup procedures to minimize BOD, fecal coliform, color, and manganese concentrations and accelerate early removal of lead in the anaerobic cell effluent.

Data from the 24-month operation of the pilot scale bioreactor showed that the biotreatment system could consistently remove total and dissolved lead to concentrations less than 0.02 ppm, despite significant fluctuations in flow and metal loading and changes in climate (rainfall and temperature).

Large Scale Design

The large scale system was designed based on the performance of the pilot scale system and the interim bench scale studies. The large scale system was estimated to cost approximately \$500,000 and require about two to three months of construction time, depending on the vagaries of weather and construction surprises. System operational costs include water quality monitoring as mandated by law. No additional costs for reagents are incurred; since the system uses gravity flow, moving parts are few and include valves, minor flow controls and monitoring devices. Based on carbon depletion rates observed in the pilot system, the anaerobic cell substrate life was projected to be greater than 30 years; the full scale biotreatment system should be virtually maintenance-free.

Should mine water quality deteriorate, the full scale design included a 50 percent safety factor. The pilot scale system was tested by operating for about 90 days at double the design capacity; compliance effluent with respect to total lead concentration and other key performance parameters resulted from this test.

Two construction sites were considered for the final system design. One site was located within the existing mine permit area, bounded by the mine/mill buildings, a pond at the toe of a tailings dam, a steep hillside, and the West Fork of the Black River, the receiving stream. This site had numerous other constraints

including multiple buried utilities, a concrete-lined drainage structure which bisected the site and an above-ground liquid propane storage tank. Relocation of either of these structures was not allowed. An alternative site was located about 2,000 feet away, on the other side of the main access highway to the mine. This relatively uncluttered site consisted of open pasture land bounded by woodland on two sides, the highway, and the West Fork of the Black River. This area, while controlled by Asarco, was not within the mine permit area. Mine water to be treated would need to be pumped to this site; the pipeline would need to be bored through the highway embankment. A regional natural gas pipeline was located within the highway right of way.

After a preliminary design analysis revealed that the full scale system could fit barely within the land available adjacent to the mine/mill buildings even considering the various constraints, the alternative site was rejected to avoid additional land disturbance, permitting delays and pumping of mine effluent.

System Dimensions

The biotreatment system is composed of five major parts (Figure 3): a settling pond, two anaerobic cells, a rock filter, and an aeration pond (Knight Piésold, 1997). The system is fully lined. The design was also integrated into the mine's pre-existing fluid management system.

- A rectangular-shaped, 40 mil HDPE-lined settling pond has a top surface area of 32,626 square feet (0.75 acres) and a bottom surface area of 20,762 square feet (0.48 acres). The sides have slopes of 2 horizontal to 1 vertical (2H:1V). The settling pond is nominally 10 feet deep. It discharges through valves and parshall flumes into the two anaerobic cells.
- Two anaerobic cells are used, each with a total bottom area of about 14,935 square feet (0.34 acres) and a top area of about 20,600 square feet (0.47 acres). Each cell is lined with 40 mil HDPE and was fitted with four sets of fluid distribution pipes and three sets of fluid collection pipes, which were subsequently modified (see Start Up discussion). The distribution/collection pipes were connected to commonly-shared layers of perforated HDPE pipe and geonet materials sandwiched between layers of geofabric. This feature of the design

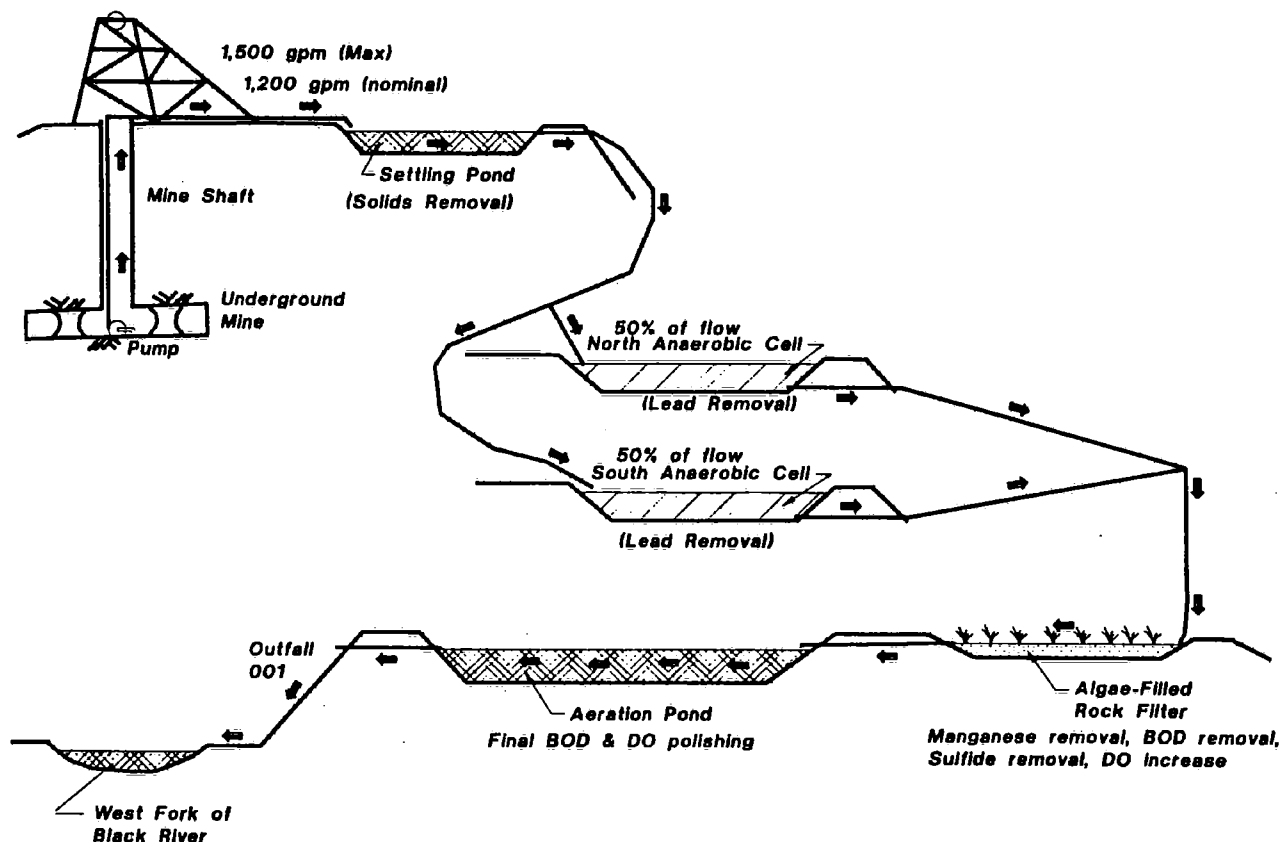


Figure 3, System Configuration

was intended to allow control of sulfide production in hot weather by decreasing the retention time in the cell through intentional short circuiting.

The spaces between the fluid distribution layers were filled with a mixture of composted cow manure, sawdust, inert limestone, and alfalfa, referred to hereafter as "substrate." The total thickness of substrate, piping, geonet and geofabric was about six feet. The surface of the anaerobic cells was covered with a layer of crushed limestone. Water treated in the anaerobic cells flows by gravity to a compartmentalized concrete mixing vault and thereafter to a rock filter cell. The gravity-driven flows can be directed upward or downward.

- The rock filter is an internally bermed, clay-lined shallow cell with a bottom area of about 63,000 square feet (1.4 acres) and a nominal depth of one foot. It is constructed on compacted fill that was systematically placed on the west side of a pre-existing mine water

settling pond. Limestone cobbles line the bottom of the cell and the cell is compartmentalized by limestone cobble berms.

- The discharge from the rock filter flows through a drop pipe spillway and buried pipe into a 40 mil HDPE lined aeration pond. The aeration pond surface covers approximately 85,920 square feet (2.0 acres). The aeration pond discharges through twin 12-inch HDPE pipes into a short channel that leads to monitoring outfall 001 and thence into West Fork.

After the water pumped from the underground mine enters the settling pond, all flows are by gravity.

Permitting Hurdles

The permitting aspects of the project were very complex. Regulators needed to be convinced that an organic-based wetland-type substrate could remove dissolved lead from mine effluent. Note: Missouri is known as the "Show Me" state and regulators were suspicious of a new and innovative technique that did not quite fit in established regulatory guidelines or statutes.

However, regulators were willing to listen to facts and the flow of communications was good. Nevertheless, cow manure as an ingredient in the anaerobic cell substrates was a special regulatory hurdle because its use raised issues of BOD, fecal coliform bacteria and other organic-related water quality criteria problems from a non-degradation of West Fork perspective.

From a construction permit perspective, only one regulation was a problem. Missouri Department of Natural Resources (DNR) regulation 10 CSR 20-8.110 [Engineering - Reports, Plans and Specifications] is for conventional water treatment plants that remediate fecal-type wastes. This regulation was not promulgated with the concept of using manure as a construction material.

Education of permit document reviewers was a key aspect of the permitting effort, supported by the results of the two years of pilot scale test results. The original permitting application was made after gathering one year's worth of pilot data; data acquisition continued throughout the permitting process. Making the permit submittal fit the regulation requirements was somewhat akin to making a round peg fit into a square hole.

Missouri DNR raised useful and valid concerns which were addressed with additional testing, including monitoring for fecal coliform, color, BOD, and other minor constituents. This additional testing raised the level of knowledge of passive treatment performance in general and improved the database utilized in the final design.

The closure and reclamation of the biotreatment system after its scheduled decommissioning at the end of the West Fork facility life was also a DNR concern. The system was constructed within the boundaries of the waste management areas as defined by the Metallic Minerals Waste Management Act and was, by definition, a waste management structure. Therefore, closure and reclamation activities would adhere to Section 5 of the Metallic Minerals Waste Management Permit issued to Asarco's West Fork Unit in January, 1991.

The substrate material, made up primarily of sawdust, alfalfa hay, limestone and cow manure, was projected to accumulate metals over time through the operation of the water treatment system. Based on average flow and metal content of the mine water, it was estimated that the final metal loading in the substrate will be 1,866 mg/kg Pb as PbS. At the end of the active life of the biotreatment system, core samples of the substrate will be subjected to TCLP. If the substrate material fails

TCLP, disposal will be in accordance with all applicable laws and regulations pertaining to characteristic hazardous waste. If the substrate passes TCLP, it will be used as an organic fertilizer to stimulate vegetation growth on the slope of a nearby tailings dam. Data from other sites have suggested that organic substrate containing metals will pass TCLP tests if it is allowed to oxidize first (McLain, 1995).

Odor control from the proposed facility was not expected to be a problem. Asarco personnel conducted a reconnaissance air quality screening study at the site with chemically activated sniffer sampling of air immediately adjacent to the operating pilot scale biotreatment plant. Hydrogen sulfide concentrations were the focus of the survey. Air quality modeling suggested that the facility would be in compliance with applicable standards.

Another point favoring its application at West Fork, the biotreatment method had been used at other Asarco facilities (in Colorado, Montana [which was issued an interim NPDES permit] and Canada) and it was accepted as a viable treatment method by agencies in other states and the USEPA. Some of the original research work into biotreatment was sponsored under the EPA's Emerging Technology Program. The following mine/mill sites are known to have included biotreatment in their record of decision:

- Clear Creek, Colorado
- Buckeye Landfill, Ohio
- Palmerton Site, Pennsylvania
- Bunker Hill, Idaho

In the cases listed above, biotreatment was the preferred alternative or a key component of the preferred alternative.

System Construction

Following permitting, the biotreatment system was constructed in accordance with plans and specifications as submitted to and approved by the Missouri Department of Natural Resources (MDNR) Water Pollution Control Program. The construction was authorized under the Construction Permit issued on March 12, 1996. Work commenced on March 13, 1996; as of July 10, 1996, the work was declared to be substantially complete in accordance with the Plans and Specifications. Wet weather delayed construction in situations requiring the installation of welded geomembrane materials. There were no change orders.

Construction management of an outside contractor was provided by an Asarco engineer and construction quality assurance was conducted by a Knight Piésold engineer. Minor field changes in the design typically improved the facility. Some of these are discussed below.

The original recipe for the substrate included aged sawdust, low-manganese limestone, aged cow manure, and alfalfa hay in decreasing proportions. As specified, the alfalfa hay was assumed to be baled. A readily-available source of slightly moldy alfalfa hay cubes was substituted as a field change. The volumetric proportions of the substrate components changed slightly (the substrate became denser) and additional sawdust was used to make up the total volumetric deficit. The addition of more organic carbon could increase projected cell life, already in excess of the required operational time.

As originally designed, the anaerobic cells would have discharged via flexible hoses into geomembrane-lined channels. These were replaced by a compartmentalized reinforced concrete vault with variable-height internal baffles. This structure in essence combined the features and intent of a specified "concrete mixing vault" with the level/flow control provided by the flexible hoses; it also took up far less space.

The construction was sequenced so that the settling pond was built and commissioned first so that the mine and mill could continue to operate during construction. Subsequently, the old settling pond was backfilled in part to become the foundation of the rock filter. The portion of the remaining settling pond was lined with HDPE geomembrane and became the aeration pond.

Start-Up Experience

Bench-scale test results suggested that the anaerobic cells be incubated with settled mine water for about 36 hours or less before fresh mine water was introduced at full flow to minimize initial levels of BOD, fecal coliform, color and manganese. For about two weeks, pumps recycled the water within the two anaerobic cells. Based on data collected in field, and subsequent laboratory confirmation, the water from the anaerobic cells was routed to the tailings pond for temporary storage. At that point, the rock filter and aeration ponds were brought on-line. In the meantime, the mine discharged according to plan through an overflow pipe from the settling pond as it had during construction

of the other components. Plumbing was available to temporarily discharge to an adjacent tailings pond, if necessary, where it would be stored for later treatment and release.

After about six weeks of full scale operation, the apparent permeability of the substrate was found to be lower than expected and the system was operating nearly at capacity. The system had been designed so that either of the two anaerobic cells could accept the full flow amount on a temporary basis in case maintenance work required a complete cell shutdown.

Research found that H_2S gas, generated by the sulfate reducing bacteria, was being retained in the substrate in the anaerobic cells; this created a gas-lock situation that prevented full design flow. A temporary solution was obtained by periodic "burping" of the cells using the control valves. However, the "burping" had to be performed at 24-hour intervals and it was determined that this solution was too labor intensive.

The sulfide gas lock problem was investigated in December, 1996 by installing vent wells in the substrate and measuring the gas pressures. Observations indicated that the gas was a factor in apparent short circuiting of the water passing through the cell. The layered geotextiles, (geonet and geofabric) originally intended to promote horizontal flow, appeared to be trapping the sulfide gas beneath them and vertical flow was being restricted. The permeability of the substrate itself was for the most part unaffected. However, construction practices in the south anaerobic cell could have contributed to the situation. Here, a low ground bearing bulldozer was used to place substrate in nominal six-inch lifts. This could have created a layering effect that may have trapped gas as well. Substrate layers in the north anaerobic cell were placed in a single lift and no layering effect was observed during subsequent excavation. It is noteworthy that the mid-cell geotextiles had not been a feature of the pilot test cell design.

The first phase of a permanent solution was implemented with a trenching machine that ripped through the geonet/geofabric layers in the south anaerobic cell. This disrupted the gas-trapping situation. Subsequently, the substrate from the entire south anaerobic cell was excavated and the cell refilled without the geotextiles in June, 1997. Identical action was taken on the north anaerobic cell in September, 1997. These actions have apparently solved the gas lock problem.

Operational Results

The average influent water quality can be compared with discharge water quality (Table 1) during the June through November, 1997 period. Discharge levels of Pb and other metals were reduced substantially from average influent levels. For Pb, the level was reduced from a typical average of 0.40 mg/L to between 0.027 and 0.050 mg/L. Zn, Cd and Cu effluent concentrations were also reduced.

Conclusions

- 1) A practical design has been developed to bring Pb values down to stringent water quality standards.
- 2) Bacterial sulfate reduction is the major Pb removal process.
- 3) An aeration step is needed to polish for Mn, BOD, fecal coliforms removal and re-oxygenation.
- 4) Pilot testing should include as many features of the final design as possible to minimize start up difficulties.
- 5) Education of regulators on innovative water treatment techniques can facilitate permit approvals.

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Table 1. West Fork Water Quality Data

Parameter	Typical Average Influent Water Quality	Range of Water Quality Discharge (June - November 1997)
Pb	0.4	0.027 - 0.050
Zn	0.36	0.055 - 0.088
Cd	0.003	<0.002
Cu	0.037	<0.008
Oil and Grease	--	< 5.0
H ₂ S	--	0.011 - 0.025
Total Phosphorus	--	<0.05 - 0.058
Ammonia as N	0.52	<0.050 - 0.37
Nitrate and Nitrite	2	<0.050 - 1.7
True Color	--	10 - 15
BOD	1.7	<1 - 3
Fecal Coliform	--	<1 - 2
pH	7.94	6.63 - 7.77
TSS	--	<1 - 4.2

Sources: Asarco, Inc., 1997, and Knight Piesold LLC, 1995.

METALS, SULFUR, AND CARBON BALANCE IN A PILOT REACTOR TREATING LEAD IN WATER

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James J. Gusek (Knight Piesold, LLC, Denver, Colorado)

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James Fricke (Advanced Geoservices Corp., Sandy, Utah)

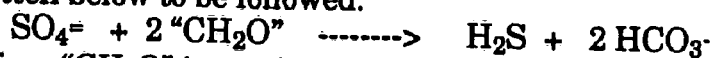
ABSTRACT: Water from an underground lead mine has pH of 8.0 with 0.4 to 0.6 mg /L of Pb and 0.18 mg/L of Zn. A pilot scale reactor using sulfate-reducing bacteria was built to remove lead to below the environmental limit of 0.030 mg/L. The system utilized 53 m³ of a mixture of sawdust, manure, hay, dolomitic tailings, and coarse mine waste. Throughout the two-year operation, the system has treated from 8 to 185 L/min of water, and lead and zinc have been reduced to below detection limits of 0.02 and 0.008 mg/L, respectively. Because pH of the water was neutral and the loading of heavy metals was low, the sulfate reduction reaction could be followed. Sulfide and alkalinity in the water increased as SO₄⁼ in the water decreased. During the summer, sulfide production reached 2 moles S⁼ produced/m³/day. In the winter, sulfide production dropped to more typical design values of 0.3 moles S⁼ produced/m³/day. This change in production of sulfide is partially attributed to the change in temperature of the water flowing through the pilot cell.

INTRODUCTION

Because of the formation of soluble neutral complexes, lead solubility in neutral to alkaline waters is often above the drinking water standard of 0.050 mg/L. In addition, normal methods of removing metals from water such as the addition of hydroxide or carbonate only make lead more soluble in slightly alkaline waters (McMillan, et al. 1994). Modelling studies suggest that one method to overcome this problem is by the addition of S⁼, which causes the precipitation of a highly insoluble sulfide. From the viewpoint of passive bioremediation, generation of sulfide through the activity of sulfate-reducing bacteria has been used in the removal of metals from water (Wildeman, et al., 1994). In most instances this type of treatment technology has been used on acidic coal- and metals-mining drainages (Wildeman, et al., 1993, 1995). However, in this study, the objective was the removal of lead from a slightly alkaline water generated from the dewatering of an underground lead mine that is hosted in a dolomitic country rock.

The site of the mine is the New Lead Belt in Missouri. The treatment objective is to reduce the lead concentration to below the water quality standard of 0.030 mg/L and insure that other contaminants are not added to the water during the treatment. Because the water was buffered by the carbonate host rock, the pH ranged from 7.9 to 8.2. The concentration of dissolved lead ranged from 0.07 to 0.12 mg/L while total lead ranged from 0.4 to 0.7 mg/L. Besides lead, the concentration of dissolved zinc and manganese ranged from 0.1 to 0.7 and 0.01 to 0.5 mg/L respectively.

This paper reports on the successful operation of a pilot cell that tested the feasibility of removal of lead through the precipitation of lead sulfide generated by sulfate reduction. In the treatment of acid mine drainage, the objective is to generate as much sulfide as possible for metals removal (Wildeman, et al. 1993, 1994). However, in this case because the water is neutral and the concentration of metal contaminants is only slightly above the environmental limits, the objective turned out to be to generate just enough sulfide to precipitate the lead and zinc. Because of the chemistry of the water and the desire of ASARCO Inc. to completely understand the chemistry involved in this passive treatment technology, chemical constituents in the water beyond the contaminant concentrations were analyzed throughout the course of the operation of the pilot cell. In particular, SO_4^{2-} , S^{2-} , alkalinity and organic content in the form of biological oxygen demand were determined on a regular basis. This enabled a more thorough analysis of the sulfate reduction equation written below to be followed.



In this reaction, "CH₂O" is used to represent organic matter.

EXPERIMENTAL DETAILS

The pilot cell was approximately 1.5 meters deep and had a working volume of 53 cubic meters. Based on laboratory studies of possible substrate materials, a mixture of sawdust, manure, hay, dolomitic tailings, and coarse mine waste was used. This mixture was inoculated with a 1:1 mixture of cow manure and saw dust that was used in a bench-scale sulfate-reducing reactor. The bench-scale system removed 0.08 mole of Pb and Cu/m³/day. Using this removal rate, the design flow rate in the pilot cell was set at 77 L/min. The pilot cell was started on March 11, 1994 and operated for over 600 days.

During the operation period, the cell was visited at least twice a month and field measurements were taken. Twice a month for the first six months and then monthly thereafter, water samples were taken. All handling, preservation, and storage protocols were followed. Analysis of water constituents were performed by the environmental labs of ASARCO Inc.

RESULTS AND DISCUSSION

During the operation of the pilot system, lead and zinc were consistently removed to below detection limits of 0.02 and 0.008 mg/L, respectively. Concentrations of the constituents that are the reactants and products of the sulfate reduction reaction reveal interesting trends. In Figure 1, is shown the change in concentration between the influent and effluent water for sulfate, S^{2-} , and alkalinity. Sulfate and S^{2-} concentrations are in units of mg/L and alkalinity is in units of mg CaCO₃/L. Figure 2 plots the S^{2-} generated within the pilot cell in units of moles of S^{2-} /m³ of substrate/day. The moles of S^{2-} generated were determined by two methods: From the reduction in the concentration of SO_4^{2-} in the effluent compared to the influent, and from the concentration of S^{2-} in the effluent. To make this calculation, it is necessary to know the volume of substrate in the pilot cell and the flow of water through the cell. In both figures, the number of days of operation is plotted on the x axis. The first summer is from day 100 to 200, winter is from day 260 to 360, the second summer is from day 460 to 560.

CHANGES IN SULFATE, ALKALINITY, AND SULFIDE IN THE ASARCO PILOT CELL WATER

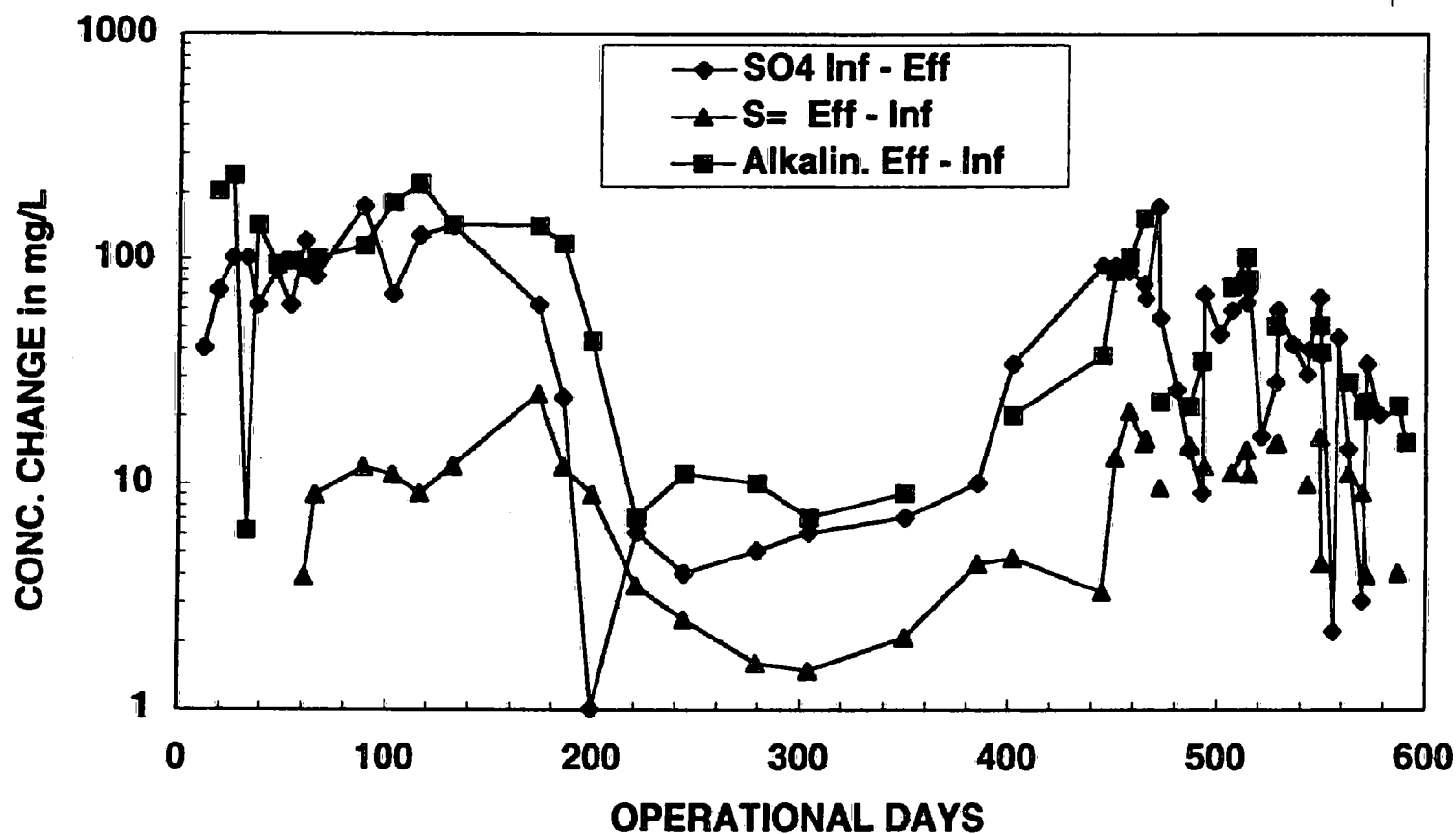


FIGURE 1. The change in concentration between influent and effluent waters in the ASARCO Inc. pilot cell. All concentrations are in mg/L.

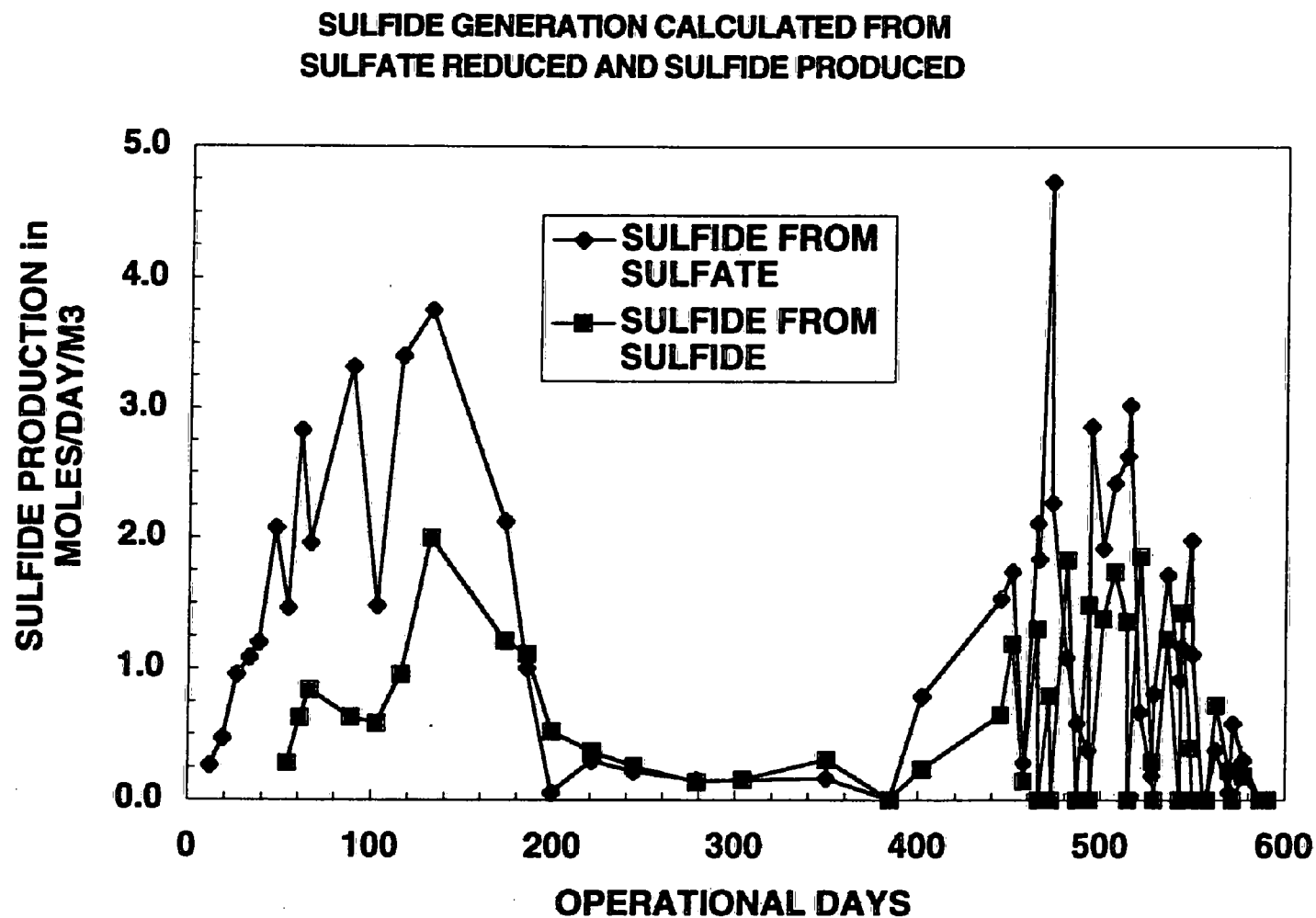


FIGURE 2. Estimates of the amount of sulfide produced in the ASARCO Inc. pilot cell. One estimate is from the change in sulfate concentration between influent and effluent; the other estimate is from the concentration of S⁼ in the effluent. Sulfide production is in moles S⁼/m³/day.

Examination of Figure 1 shows that, in a broad fashion, the reduction of SO_4^{2-} in the water correlates with an increase in alkalinity and S^{2-} . This is what would be expected by the sulfate reduction reaction. On a mole basis, 96 mg/l of SO_4^{2-} reduced would generate 200 mg CaCO_3/L of alkalinity and 32 mg/L of S^{2-} . Taking this into account, if the reduction of SO_4^{2-} in the water is due only to sulfate reducing bacteria, then one would expect the alkalinity and S^{2-} produced to be higher than what is shown in Figure 1. It would be most surprising if the changes in concentration of all three constituents were caused solely by the sulfate reduction reaction.

With respect to alkalinity, the pH of the water drops from an average of 8.0 to values between 6.5 to 7.0 in the summer and 7.0 to 7.4 in the winter. Although unraveling carbonate chemistry in water is complex, it appears that some of the alkalinity produced may be used to neutralize acids produced in the pilot cell. Because this pH drop is seasonal, it may be caused by other biologic reactions that are accelerated in the summer. With respect to S^{2-} , because the concentrations of heavy metals in the mine water are low, little S^{2-} is lost through the precipitation of sulfides. However, because sampling and preservation for S^{2-} is complex, low concentration values are not surprising.

In Figure 2, based on the previous discussion, S^{2-} generation calculated by sulfate reduction can be considered to be an upper estimate while sulfide generation calculated from S^{2-} concentration in the water is a lower estimate. In previous projects, 0.3 moles of S^{2-} produced/ m^3/day calculated from sulfate reduction has been used as the design rule of thumb. In this system, values of sulfide generation of 3 to 4 moles of $\text{S}^{2-}/\text{m}^3/\text{day}$ were achieved. Even if the more conservative estimates based on S^{2-} in the water are used, the summer production values often reached 2 moles produced/ m^3/day . Such high levels of sulfide production in a passive system were surprising.

Because sulfide in the water is not desirable, the flow of water through the system was increased to 185 L/min, more than double the design value. This dropped the concentration of S^{2-} in the water but it did not decrease the generation of S^{2-} within the substrate. In the first summer, some of the highest values of S^{2-} production were achieved at the highest flow rates.

The first reason why the rate of sulfide production might be quite high is because, in this system, slightly alkaline water is being treated. A common sulfide production value used is 0.3 moles of $\text{S}^{2-}/\text{m}^3/\text{day}$ (Wildeman, et al., 1993, 1994). However, this value was generated through experiences in the treatment of acidic waters whose pH ranged from below 3 to about 4. In this study, the pH of the water averages 8.0 which is within 6 to 9, the optimum pH range for sulfate reduction.

In the first summer there were large quantities of mobile organic material readily available for the sulfate-reducing bacteria. This was monitored through the measurement of the biologic oxygen demand that was between 200 and 400 mg/L in the first 60 days of operation and averaged 50 mg/l during the summer months. It was assumed that this low molecular weight organic material was fueling the metabolism of the sulfate-reducing bacteria. This hypothesis seemed to be confirmed by the fact that on about the 200th day of operation, the BOD fell to around 1 mg/L and sulfide production dropped to below 0.5 moles of $\text{S}^{2-}/\text{m}^3/\text{day}$. However, during the second summer, the rates of production again rose to 2 moles of $\text{S}^{2-}/\text{m}^3/\text{day}$.

Because the rate of production of sulfide shows a seasonal trend, an alternative explanation for the changes is the temperature of the pilot system. To reduce suspended solids, the water from the mine enters a settling pond and the water for the pilot cell is taken from this pond. Because of this, the temperature of the influent ranges from 6 °C in the winter to 26 °C in the summer. The temperature of the effluent is always within 1 °C of the temperature of the influent. The temperature dependence on the rate of sulfate reduction in bioreactors has been noted before (Wildeman et al., 1995). The interesting result in this study is that rates of sulfide production appear to be able to reach values of 2 moles of $S^{2-}/m^3/day$ when the reactor temperatures reach 25 °C. Such large variations in the rate of S^{2-} production are an important factor to consider in the design of sulfate-reducing wetlands and bioreactors.

CONCLUSIONS

The results of this pilot-scale project on the treatment of lead in water through sulfate reduction has produced the following conclusions:

- Consistent treatment of lead and zinc in circum-neutral water to below environmental limits is possible.
- The sulfate-reduction reaction can be followed by the changes in sulfate, alkalinity, or S^{2-} in the water.
- Sulfate reduction appears to be quite dependent on the temperature of the reactor. The production range appears to be from below 0.3 moles of $S^{2-}/m^3/day$ when the temperature is below 10 °C to above 2 moles of $S^{2-}/m^3/day$ when the temperature is above 25 °C.

Based on the results of the pilot-scale study, a full-scale system capable of treating 1,500 gpm has been built and is in its first year of operation.

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MITIGATION OF WATER CONTAMINATION AT THE HISTORIC FERRIS-HAGGARTY MINE, WYOMING

(Pilot)

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J. J. Gusek

Knight Piésold LLC
Denver, CO

For presentation at the SME Annual Meeting
Orlando, Florida— March 9-11, 1998

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